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Stephen R. Leone

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University of California - Berkeley
Sponsored Projects Office
2150 Shattuck Avenue
Suite 313
Berkeley, CA 94704-5940

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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Dr. Michael R. Berman
AFOSR/NL
875 Randolph St., Suite 325   Room 3112
Arlington, VA 22203-1954

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14. ABSTRACT
This research program explored time-resolved dynamics of molecular systems by femtosecond photoelectron spectroscopy using high order harmonics. Ultrafast soft x-ray laser pump/probe studies revealed changes in binding relations and atomic core level shifts in the molecules during chemical rearrangements by detecting the changes in photoelectron energies as a function of internuclear separation in dissociative states in real time. Harmonic pulses with photon energies up to 100 eV and femtosecond time resolution were produced with excellent efficiency and pulse-to-pulse stability. Valence and core photoelectron spectra were obtained on neutral atoms and molecules. Phase manipulation of high order harmonics was achieved. Photoelectron spectra and photoionization mass spectra of gas phase ionic liquids were obtained. Two color excitation spectra of bromine molecules were investigated, as well as Rydberg wave packet photoelectron angular distributions. Pump/probe experiments on the photodissociation of metal carbonyls, halogens, and aluminum halides were also under investigation.

15. SUBJECT TERMS
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"Ultrafast Soft X-Ray Probing of Core Level Molecular Dynamics"

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Final Performance Report

Stephen R. Leone - Principal Investigator
Department of Chemistry
University of California
Berkeley, California 94720

Executive Summary

This research program explores the time-resolved reaction and fragmentation dynamics of diatomic and polyatomic molecules using femtosecond valence and core level photoelectron spectroscopy.[1-11] The chemical shifts in the electron energies provide direct information about the changes in electron orbital configurations as a function of internuclear separation in dissociative states of these molecules. Ultrafast soft x-ray laser pump/probe experiments take advantage of the femtosecond time resolution capability of a novel high order harmonic x-ray source by detecting time resolved valence electrons and atomic core level shifts in excited species as well as changes in the photo-ion mass distribution during chemical rearrangements. The experiments probe time-resolved valence (PES) and core level (XPS) spectroscopies on excited states and during photofragmentation of simple diatomics, metal halogen, and carbonyl species, as well as intramolecular processes in polyatomic molecules. The apparatus produces high order harmonics of a Ti:sapphire laser in the x-ray region of the spectrum with ultrafast pulse durations and is used to measure valence orbitals and atomic core levels during reactions and dissociation. The instrument consists of a 2.5 mJ pulse energy, 1000 Hz repetition rate Ti:sapphire laser system, a 1000 Hz pulsed jet of rare gas species for harmonic generation, harmonic separation by grazing incidence gratings, a vacuum chamber for sample introduction, and a magnetic bottle time-of-flight electron spectrometer, and a velocity map imaging system, for kinetic energy analysis of the resulting photoelectrons. High order harmonics of the Ti:sapphire laser up to the 65th ($\approx$100 eV) are produced with good efficiency. Ultraviolet and soft x-ray (core level) photoelectron spectra are obtained on a large variety of neutral atoms and molecules in this table-top laboratory setup. The first detailed ultrafast pump-probe experiments were performed upon a dissociative state of Br_2 molecules.   These are extended to studies on metal carbonyls. Signal background analysis and subtraction permits small fractional changes in the photoelectron spectra as a function of time to be observed. A wave packet on a dissociative state is observed by this method. Other experiments investigate phase shaping of the harmonics themselves, the preparation and measurement of Rydberg wave packets, and the imaging of time-resolved angular distributions of photoelectrons from wave packet motion. In addition, related experiments combine synchrotron radiation in the VUV and soft x-ray regime with pulsed laser excitation for two-color and high-resolution characterization. Finally, the photoelectron spectra and photoionization mass spectra of gas phase beams of ionic liquids are obtained.

Executive Summary con't.*

Publications:

D. Strasser, T. Pfeifer, B. J. Hom, A. M. Müller, J. Plenge, and S. R. Leone, "Coherent interaction of femtosecond extreme-UV light with He atoms," Phys. Rev. A **73**, 021805 (2006).

K. L. Knappenberger, Jr., S. Gilb, V. G. Stavros, E. W. Lerch, E. A. Torres, D. Strasser, L. Lau, and S. R. Leone, "Ultrafast Wave Packet, Coherent Control and Dissociation Dynamics," Femtochemistry VII: Fundamental Ultrafast Processes in Chemistry, Physics, and Biology; A. W. Castleman, Jr. and M. L. Kimble, Eds.; Elsevier: Amsterdam 14 (2006).

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*The move of the principal investigator's laboratory from the University of Colorado, Boulder, to the University of California, Berkeley, created the absence of publications in 2004 and 2005.

Final Report

Recent developments in the generation of high-order harmonics[12-16] with femtosecond laser pulses in rare gases offer excellent opportunities for the experimental investigation of time-resolved valence- and core-level spectroscopy of dynamical processes in atoms and molecules. Until recently, these laser sources were primarily investigated by groups working on the harmonic generation process itself. Now these tools can be used to address a number of intriguing chemical and materials problems of wide interest. High harmonic sources can now produce up to 1000 eV photon energies,[15] attosecond pulses,[17-19] and can generate photon fluxes of as high as 1 nJ per harmonic per pulse,[20,21] depending on wavelength. In work here, lower harmonics, with narrower bandwidths, up to 100 eV are used; these are also referred to as EUV and XUV wavelengths.[22] In this proposal the term soft x-ray is used throughout. This final report provides (A) brief highlights of the instrumentation developed in this laboratory for ultrafast soft x-ray probing of molecular dynamics and then (B.1 – B.8) describes the results of recent investigations.

A. Apparatus for Ultrafast Soft X-Rays

The apparatus constructed for ultrafast soft x-ray research is illustrated in Fig. 1.[1] It consists of a 1000 Hz Ti:sapphire laser that produces 2.5 mJ per pulse at 800 nm with pulses of 70 fs duration, a piezoelectric pulsed valve, also operating at 1000 Hz, to form the jet of high density rare gas that is used for the harmonic generation, a vacuum chamber to introduce gaseous samples, and a time-of-flight magnetic bottle photoelectron spectrometer. The apparatus incorporates frequency doubling and tripling of the Ti:sapphire fundamental pulse in nonlinear crystals to generate a separate photolysis pump pulse, which is sent through an optical temporal delay line. Two

Figure 1. Apparatus for generating high order harmonics for photoelectron spectroscopy and pump/probe time-resolved studies with soft x-ray harmonics.

grazing incidence gratings are used to select individual harmonics and to recompress the x-ray pulses (see Fig. 1).

The philosophy in constructing the apparatus was to make a reliable source of femtosecond soft x-rays that operates at high repetition rate (1000 Hz). There is a tradeoff
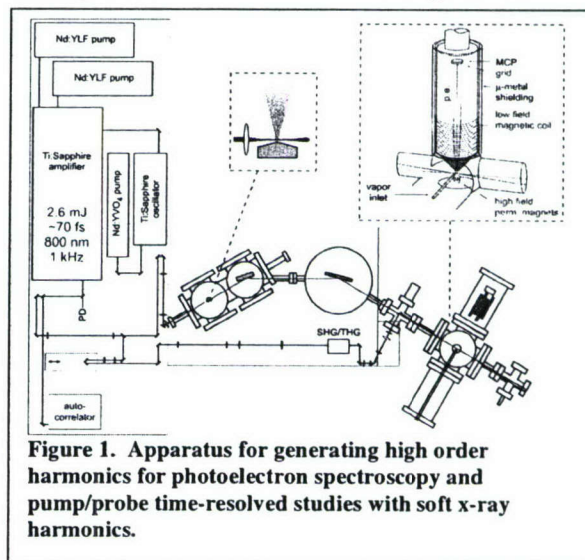
between obtaining the shortest possible pulse duration or shortest possible harmonic wavelength versus reliability and bandwidth. It is necessary for the system to operate indefinitely and on a daily basis in order to make all the necessary x-ray on vs. pump on/pump off and pump only experiments to obtain the small differential signals with high accuracy. In recent experiments, two spectra can be subtracted to obtain 1 part in 10^4 differential signals. This necessitates a stable Ti:sapphire laser system, consisting of a seed laser, regenerative amplifier, and two-pass amplifier. In order to obtain small spectral bandwidths of the harmonics for photoelectron spectroscopy, a longer pulse of 70 fs was chosen; bandwidths of 0.1-0.4 eV are routinely achieved[2] for individual harmonics to obtain good resolution in the photoelectron spectra.

For the production of high order harmonics in rare gases, the laser is focused to 10^{14}-10^{15} W cm^{-2} in a high density of a rare gas ($\approx 10^{18}$ cm^{-3}) in a pulsed jet. Semiclassically, the process involves driving an electron away from the ionic core of the rare gas and then, on the opposite cycle of the light, driving the electron back into the core, whereupon the harmonic light is generated by the interaction of the returning electron with the core.[13] The light is produced with good efficiency over a large number of odd harmonics up to a cutoff energy (Fig. 2). The odd harmonics are produced,

Figure 2. High harmonics generated in neon and argon. Note the lower energy cutoff in argon and the overlapping orders of the grating in the neon spectrum.

resulting from symmetry in an isotropic medium. With this apparatus, harmonics of 800 nm light are produced up to the 65th ($\approx$100 eV) in Ne and excellent static photoelectron spectra are obtained with excellent signal-to-noise (100:1 in minutes).[4] For pump-probe experiments, often the signal-to-noise ratio must be on the order of 10000 or higher to obtain the desired differential changes in the photoelectron spectra. Details about the generation and optimization of the high harmonic process were investigated, including tuning, pulse duration, bandwidth, and the effect of pulse chirp on the harmonic spectra[4] (chirp is the process where the frequency of the ultrafast pulse sweeps from high to low or low to high over the duration of the pulse).

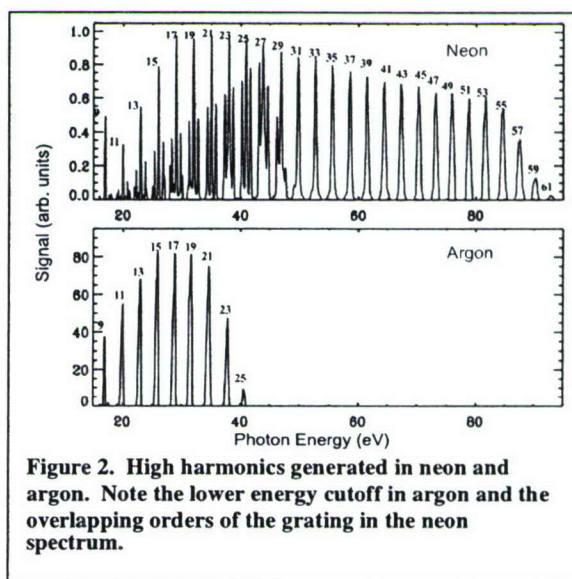The magnetic bottle time-of-flight electron spectrometer,[24-27] based on a design of Neumark and co-
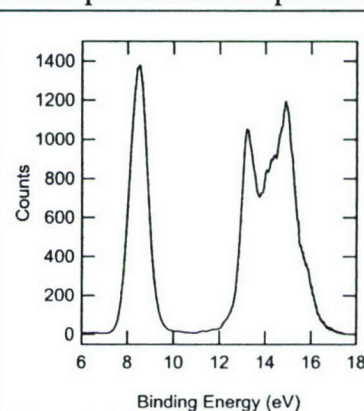

Figure 3 Photoelectron spectrum of W(CO)$_6$ taken with the 15th harmonic of the Ti:sapphire laser. The peak at 8.5 eV is due to W atoms, and the peaks at 13-16 eV are the carbonyls.

workers,[26] (Fig. 1), incorporates a modification to shift the kinetic energies of the electrons from high to low values by a retarding grid system[24,27] to obtain high kinetic energy resolution even for high velocity electrons. The advantages of this system are the ability to collect a large solid angle of the emitted electrons and the elimination of stray electron signals by confining the zone of collection to a very small region around the high field magnets. Figure 3 shows an example of a photoelectron spectrum of a complex molecule, $W(CO)_6$. The intrinsic resolution of this magnetic bottle is measured to be $\Delta E/E$ of 4%.[2,4]

B. Recent Results of Ultrafast Soft X-Ray Photoelectron Probing

Below are described selected recent results of experiments performed during the grant period.

1. Phase-shaping of soft x-ray pulses

Several methods are used to find the time and spatial overlaps of the soft x-ray pulses with visible or ultraviolet pump pulses. This is one of the challenging tasks to obtain ultrafast photoelectron signals. One method used before is to detect the overlap by "above threshold ionization" in a gas,[1,4,28,29] which results by the combination of the pump pulse during ionization by the high harmonic pulse. However, this has the drawback that the pump pulse must be focused very strongly to achieve the ATI signal, and then the conditions to use the same pump pulse for molecular excitation and dissociation lead to multiphoton processes. Another, more sensitive method recently explored in this laboratory involves excitation of a resonance in an atom, for example using the 15th harmonic to excite first the $1s^2$ to 1s3p resonance in He gas and then to ionize the excited 3p state by an 800 nm, 400 nm, or 266 nm photon.[6] The observed double resonance signal also extends the possible implentations of the soft x-ray pulses to excitation as a pump photon, not only as a probe. In He the overlap of the two pulses, temporally and spatially, is detected readily. It was

Fig. 4 Phase shaping of soft x-ray pulses around a He resonance, as a function of He pressure. The visible 402.5 nm pulse is delayed after the soft x-ray 15th harmonic.

expected that the signal would be a step function increase as a function of pump-probe delay, followed by the decay due to the lifetime of the He 1s3p excited state. At very low pressures of He this is what is observed. However, at higher He pressures, the signal (Fig. 4) contains unexpected oscillations and a rapidly decaying amplitude. We made estimates to determine
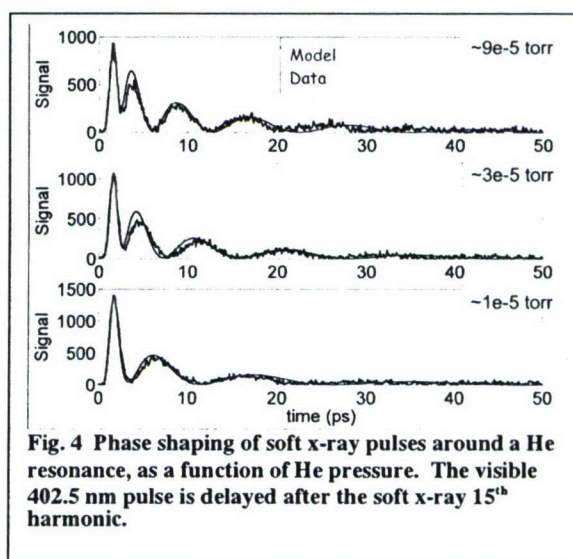
whether this unusual signal (Fig. 4) could be due to effects such as precession of the orbital in the magnetic field of the photoelectron spectrometer or dephasing of a quantum beat superposition. However the timescales for both these effects are completely inconsistent with the observed signals and the lifetime of the He 1s3p state.

By reconfiguring the apparatus to introduce a separate defined path length and pressure of He gas prior to the pump-probe "detection" in the interaction region of the magnetic bottle time-of-flight spectrometer, detailed measurements of the signals were made at various pressures. From these data it was found that the oscillatory, decaying signals arise because of phase-shaping of the soft x-ray pulses by the dispersion relationship around the resonance in the atoms. The light on the resonance itself is strongly absorbed in the first small path length of gas, and the remaining nonresonant spectral components of the soft x-ray light are modified by the negative and positive dispersion relationships around the resonance. In the well-defined experiments shown in Fig. 4, the 15th harmonic of 805 nm is used to tune to the He $1s^2$ to 1s3p resonance, and a 402.5 nm probe pulse is used to ionize the transient amplitudes of He excited state that are produced by the nonresonant components of the soft x-ray pulses. In Fig. 4 a model for the phase-shaping of the soft x-ray light is also overlaid on the data, simply based on the time evolutions of the phase-shaped soft x-ray pulses obtained by using the dispersion relationships. The modeled fits are in excellent agreement with the data. An important finding is that the transient quantum mechanical amplitude of the He 1s3p excited state that is produced by the nonresonant components of the light acts as a fast-response detector for the phase-shaped pulse. This method can now be used to investigate pulse durations and phase shapes of pulses in the soft x-ray regime, as well as to control the transient excitation amplitudes with ultrafast soft x-ray pulses. It will also be interesting to consider the possibility of phase shaping around an atomic core level near edge resonance at higher photon energies.

2. Detection of a wave packet on a dissociative state

A second challenging aspect of the pump-probe experiments is to obtain sufficient count rates and uniformity in the spectra to be able to subtract spectra with the pump on/pump off to obtain very small differential photoelectron signals. This has been a significant problem because the desired signals are always on top of an enormous parent molecule background. In addition, the pump pulse can often produce electrons by multiphoton ionization, which obscure the desired results. In recent experiments, accurate background subtraction has now been achieved in experiments on the dissociation of bromine molecules.[30] With removal of the parent background, it is now possible to quantify the depletion signal for the fraction of Br_2 molecules that are dissociated, to accurately observe the appearance of atoms and all their ion states, and to characterize the transient wave packet on the dissociative state (Fig. 5). In the most general case,

what is required is an accurate measure of the electron counts versus kinetic energy for the x-ray probe with the pump pulse on and off. However, the pump pulse can also produce multiphoton ionization by itself, and therefore these counts must also be measured and subtracted when necessary.

In the experiments, a 400 nm pump pulse is used to dissociate Br_2 through the $C^1\Pi_u$ dissociative state and the soft x-ray pulse at the 15th harmonic probes the dissociation process. The data in Fig. 5, free of the obscuring parent molecule ionization peaks, shows clear ionization signals of the atoms into multiple final atomic ion states ($^3P_{2,1,0}$ and ^1D), and the ionization of the wave packet on the dissociative state is readily detected (see caption for details). The quantitative depletion of the parent

Fig. 5 Differential photoelectron spectra of Br_2 dissocation. The depletion of the Br_2 molecules is observed through the Br_2^+ X and A ion states at 11 and 13 eV, respectively. the appearance of atoms is at 12 eV ($^3P_{2,1,0}$ ion states) and also at 13.5 eV (^1D ion state), and the signature of ionization of the dissociative state wave packet is observed in several places between 8-10 eV.

molecules is now obtained from the negative-going peaks in the differential spectrum, permitting measurements of the relative cross sections for the Br_2 and Br atoms. In this case the cross sections are found to be very similar in magnitude, whereas in earlier experiments, such high intensities of 400 nm light were required to detect the signals that the estimates of the relative cross section for the atoms compared to the molecules was too large, most likely affected by multiphoton processes. In the same spectral region of 400 nm, there can also be some excitation to dissociative curves of other electronic states, the $A^3\Pi_{1u}$ and $B^3\Pi_{0^+u}$ states,[31] and finer details of the excitation to these states may eventually be unraveled when shorter laser pulses become available. The new results indicate that it will be possible to probe small differential changes in the photoelectron kinetic energy distributions for other molecular systems.
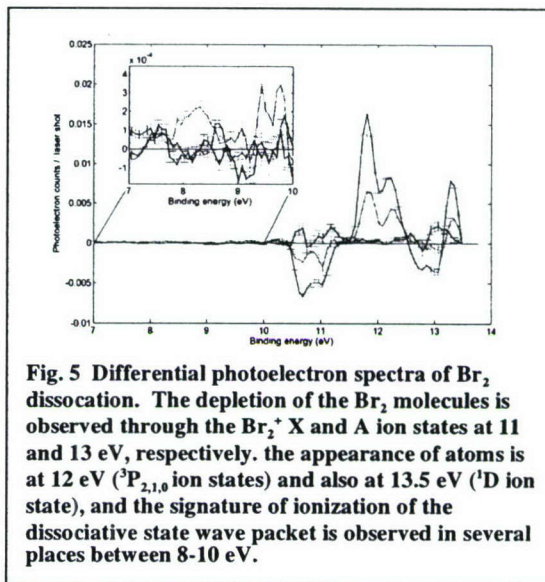
3. Two-color photoelectron spectroscopy of a Br_2 excited state

A variety of two-color pump-probe experiments are anticipated with the ultrafast soft x-ray probe instrumentation. In order to obtain baseline data for certain systems that will be the subjects of investigation, new experiments were developed at the Advanced Light Source synchrotron facility to establish two-color probing of well-defined vibrationally excited electronic states. The first of these is the excitation of Br_2 to the $B^3\Pi_{0^+u}$ state in vibrational levels v'=28 and 29 with a 527 nm Nd:YLF laser.[10] Since these states are stationary states, the timing of the pulsed laser and the synchrotron output is not consequential, yet the signals arising from these electronically excited states are readily distinguished by the kinetic energy of the outgoing photoelectrons on a velocity map imaging detector available at beamline 9.0.2.[32] Figure 6 shows the photoelectron kinetic energy distributions for a series of measurements at 9 different total energies, increasing from 10.8 eV to 12.5 eV, i.e. (a) 10.8 eV, (b) 10.9 eV, (c) 11.1 eV,

Fig. 6 (dotted lines) One color ionization of Br_2 ground X state. (solid lines) Two color ionization through the Br_2 B state. See text for total energies.

(d) 11.5 eV, (e) 11.8 eV, (f) 12.0 eV, (g) 12.25 eV, and (h) 12.5 eV. The dashed line is for the single photon ionization with the VUV light source alone and the solid line is for the same total energy, but by combining the 527 nm light with the synchrotron radiation. In the single photon data (dotted lines) it can be seen that essentially a single peak moves to higher outgoing electron kinetic energies as the energy of the photon is increased. However, in the case of the 527 nm + VUV light, there are two peaks. The origin of the high and low velocity electrons is shown theoretically[10] to arise explicitly from the inner turning point and mid-range internuclear separations, respectively, of the ionization of the excited v'=28,29 states in the electronically excited $B^3\Pi_{0^+u}$ state of Br_2. The single peak in the case of the one-photon ionization comes from the single localized wave function near the bottom of the potential well in the $X^1\Sigma_g^+$ ground state of Br_2.

Fig. 8 Core level photoelectron spectra of (a) $AlBr_3$ and (b) Al_2Br_6 with tentative assignments.

Fig. 7 Structures of Al_2Br_6 and $AlBr_3$.

4. Core level spectroscopy of $AlBr_3$ versus Al_2Br_6 In preparation for pump-probe experiments on aluminum bromide species, a series of experiments were performed to obtain the valence and core level photoelectron spectra of $AlBr_3$ and its dimer Al_2Br_6 at the Advanced Light Source.[11] In this section we discuss only the core level data, taken with 90-95 eV photon energies. A Scienta electron energy analyzer, available at beamline 10.0.2,[33] was used for these investigations, and a simple heated sampl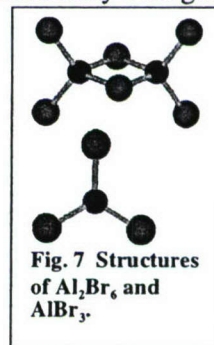e cell was used to introduce the Br–Al–Br bridge-bonded dimer (Al_2Br_6) and to dissociate the dimer to monomers ($AlBr_3$) (structures shown in Fig. 7). Figure 8 shows the spectra that were obtained with a likely set of assignments. The bridge-bonded Br atoms appear to be shifted to higher binding energy. An analysis is in progress to consider the degree of shift with regard to the unique properties of the three-center two-electron bridge bonds involving Al-Br-Al. In this three-center bridge bond a deficiency of electrons most likely causes a change in the orbital structure, and the shift. One aspect of the results in the Fig. 8 is that the Al peaks are not shifted appreciably. It will also be interesting to consider whether any of the cross sections of the atoms are altered or not. This can occur if there are changes in the core level cross sections due to strong localized shape resonances in the continuum.[34] It appears that the cross sections of the bridge-bonded and terminal-bonded atoms are similar, preserving the 2:1 ratio of terminal and bridge-bonded atom signals. It is clear that even in this simple system the analysis of the bonding is subtle, and more work is required to make a complete interpretation. A combination of additional calculations and time-resolved experiments of the bond-breaking may provide a more clear means to identify which atoms are involved in the several spectral features.

5. Rydberg wave packets in Kr atoms

During alignment of the x-ray pulses with various-wavelength pump pulses (e.g. 266 nm), it is sometimes valuable to first find the overlap of the main 800 nm pulse with the 266 nm pulse by multiphoton pump-probe ionization of Kr atoms. Oscillations in the photoelectrons were observed in the pump-probe, time-resolved signals, arising from a total energy of three 266 nm photons + one 800 nm photon (3+1').[4] The oscillations are due to the formation of wave packets

Fig. 9 Quantum beats of a Rydberg wave packet formed in Kr atoms by 3x266 nm, showing assignments and several previously unobserved 7g states.

among the Rydberg states of the Kr atoms, produced by the three photon 266 nm excitation, followed by time-delayed probe ionization at 800 nm of the wave packets. The oscillations, therefore, represent quantum beats between pairs of levels in the superposition of the wave packet states (Fig. 9). Since the magnetic bottle spectrometer in the AFOSR apparatus would distort the energy levels of the Rydberg states, a linear time-of-flight spectrometer, constructed for another project, was used for additional investigations. The support for the published investigations[7] was therefore derived jointly from both AFOSR and other grant support.

The high field of the focused 266 nm pulse causes a Stark shifting of the Rydberg levels during the laser pulse. One important result is that states that are shifted by as much as 3000 cm^{-1} below the energy of the three-photon excitation are observed in the superpositions, depending on the three-photon pump intensity, from 10-65 TW/cm^2. By varying the power density of the 266 nm laser pulse, broad regions of different Rydberg states can be excited, corresponding to principal quantum numbers n=5-10, and including s, d, and g Rydberg states. An important result is that the coherent superpositions are clearly formed during the Stark shifting process and are also preserved in the atoms when the laser field diminishes.[7]

Even though an enormous number of states are excited simultaneously, high resolution detection and assignment of the quantum beats is possible. This is accomplished by resolving narrow slices of the outgoing electron kinetic energies, essentially a post-filtering of the detected states. Thus, narrow slices of outgoing electron kinetic energies are used to determine, by selection of the final states reached by the 800 nm probe pulse, the quantum beat states that are analyzed.[7,9] In many cases the quantum beats would not be distinguishable at all because of the large number of overlapping quantum beats, but the kinetic energy resolution permits detailed extraction of the information. Fig. 9 above shows one example of the wave packet quantum beats, out of many observed, with assignments. Assignments of many previously unobserved 7g states are made,[7] and measurements of their quantum defects are obtained. As expected, the quantum defects of the g states are small, since the electrons from g states do not penetrate significantly to the atomic core of the atoms.

6. Photoelectron angular imaging of Rydberg wave packets

A velocity map photoelectron imaging system[35] was constructed for the AFOSR project, and with minor modification this imaging system was fitted to the linear time-of-flight spectrometer described in section 6 above. The imaging system was used for the first time to observe time-resolved angular distributions of photoelectrons from electronic wave packets.[8,9] This was also a cooperative venture among several people in the group, and the support for this project was therefore derived jointly from AFOSR and other grant support.

To accomplish this experiment, superpositions of only two states at a time were excited and probed. Various pairs of levels were measured. Many of the pairs showed intricate photoelectron angular distributions, as well as changes in the angular distributions. One pair of states, a 5d-8d Rydberg superposition:

$$C_1 \, 5d'[5/2]_3, \, M=0 + C_2 \, e^{-i\Delta\omega t} \, 8d[1/2]_1, \, M=0$$

where C_1 and C_2 are the coefficients of the superposition, showed a dramatic change in the

electron angular distribution that could be interpreted.[8,9] The angular distribution oscillates between a $Y_{3,0}$ spherical harmonic and a $Y_{3,\pm1}$ spherical harmonic, as a function of time. A basic image at the starting delay time, where the 266 nm pump and 800 nm probe are barely overlapped, is shown in Fig. 10. At other time delays, clear additional lobes are observed and the image oscillates. The results represent the first observation of changes in a photoelectron angular distribution as a function of a wave packet motion, in this case for a Rydberg electronic state wave packet.

Fig. 10 Photoelectron angular image from a Kr wave packet between a 5d-8d pair of states at a starting time delay of -0.39 ps.

Notably, the only way the oscillation between the $Y_{3,0}$ and $Y_{3,\pm1}$ spherical harmonics for the outgoing electron wave can occur is if the inner core angular momentum and the outer electron angular momentum are coupled, resulting in entanglement between the inner core and the outer electron wave functions. The detection of the entanglement is a significant discovery, which could not be observed without photoelectron angular resolution.

7. Time-resolved photoelecton spectroscopy of cyclopentadienyl dicarbonyl iron dimer

Figure 11 shows results of an ongoing investigation of a metal carbonyl dimer, $[CpFe(CO)_2]_2$;[36] the dissociation is being studied with pump-probe PES. This molecule is excited with 400 nm pulses, and a differential change in the PES is observed, showing the feasibility of the experiments. However, some multiphoton ionization also occurs with the 400 nm alone
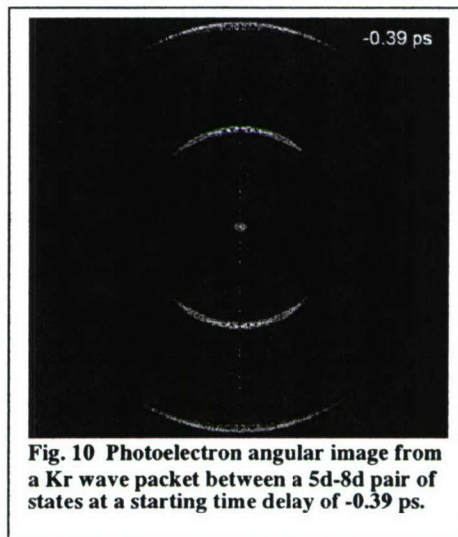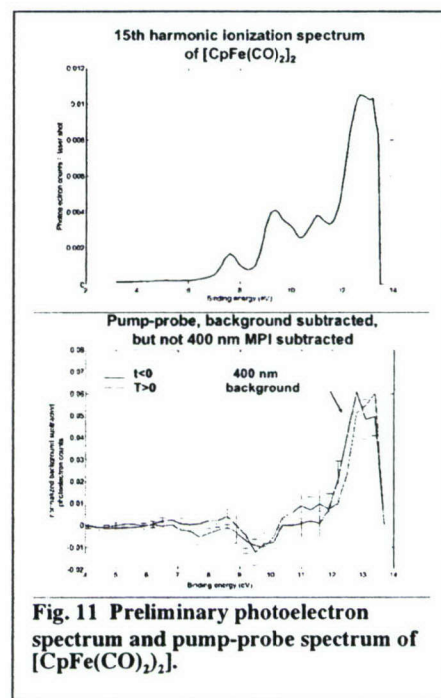
Fig. 11 Preliminary photoelectron spectrum and pump-probe spectrum of $[CpFe(CO)_2]_2$].

in the 12-14 eV region, which makes the results very preliminary. Investigations have also been initiated on $W(CO)_6$ (Fig. 3).

8. Ionic Liquids

Recently, Earle *et al.*[37] demonstrated for the first time distillation of several aprotic room temperature ionic liquids (RTIL). Following that work, which demonstrates thermal vaporization without decomposition of ionic liquids, we were able to construct an efficient source of ionic liquid beams for gas phase experiments. The source was successfully installed in our apparatus and operated with a sample of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM][Tf_2N] RTIL. The transport of ionic liquid vapor without decomposition was verified by ^1H and ^{19}F NMR spectroscopy of recondensed vapor. The addition of a time-of-flight mass spectrometer to our experimental setup, interchangeable with the photoelectron spectrometer, allows us to obtain photo-ion mass spectra of ionic liquid vapor when ionized with the high harmonics, which is found to consist predominantly of the cation mass 111 amu. The detection of the intact cation mass is an important finding since it confirms the aprotic nature of the species involved in the vaporization process. As the presence of the anion in the beam is confirmed by the subsequent NMR spectroscopy of the collected vapor, we tentatively identify the vapor as bound ion and counter-ion pairs that dissociate after ionization with high harmonics into an intact $EMIM^+$ ion (detected in our experiment) and a neutral Tf_2N fragment (not detected at this stage). Further studies of [EMIM][Tf_2N] vapor photoelectron spectroscopy with the 17th harmonic were performed. The measured valence binding energy spectrum was found to exhibit three main peaks, which correspond to binding energies of 11.4 eV, 15 eV and 20 eV. The threshold for ionization was fitted to a binding energy of 8 ± 0.1 eV. These first gas phase measurements of ionic liquid vapor will help benchmark and tune theoretical RTIL structure calculations.

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Professional Personnel Associated with the Research

Stephen R. Leone

Post-doctoral Research Associates
Daniel Strasser
Fabien Goulay
Astrid Müller
Jürgen Plenge

Graduate Students
Brian J. Hom
Louis Haber
James Clark

Publications:

D. Strasser, T. Pfeifer, B. J. Hom, A. M. Müller, J. Plenge, and S. R. Leone, "Coherent interaction of femtosecond extreme-UV light with He atoms," Phys. Rev. A **73**, 021805 (2006).

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Interactions/Transitions:

- Discussions with Steve Chambreau (from Edwards Air Force base propellants division) about design of vapor phase experiments to examine the ignition mechanism of high energy room temperature ionic liquids (RTIL).

- Discussions and exchange of ideas with Rainer A. Dressler (from Air Force Research Laboratory, Space Vehicles Directorate) about applications of RTIL and experiments with RTIL vapor, photoelectron spectroscopy and mass-spectroscopy of $[Emim][NtF_2]$.

- Collaboration with Edward J. Maginn (from Department of Chemical and Biological Engineering, University of Notre Dame, Indiana) comparing predictions of model calculations to experimental observations of RTIL vapor.

New discoveries, inventions, or patent disclosures
None

Honors/Awards
S. R. Leone
    2005 Peter Debye Award of the American Chemical Society
    Member – National Academy of Sciences
    Fellow – American Physical Society
    Fellow – Optical Society of America
    Fellow – American Association for the Advancement of Science
    Fellow – American Academy of Arts and Sciences
    Centennial Lecturer of the American Physical Society